

Beamline 6.3.1

Calibration and Standards, EUV/Soft X-Ray Optics Testing, Solid-State Chemistry

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Development and Evaluation of a New Liquid Cell System for Soft X-Ray Absorption Experiments

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INTRODUCTION

Soft X-ray is well used as a means available to investigate the electron state of valence band in a material, because the energy of soft X-ray is close to that of the valence band and strongly affects the material in the electronic state. The soft X-ray absorption spectrum provides information on the electron states between the absorbing atom and neighboring atom(s) in a material, in addition, the researches by the soft X-ray absorption spectroscopy are extensively developed with the increase of the number of the target atoms for the researches, because the elements absorbing the soft X-ray include not only the light elements, but also the elements which can cause the L- and M-shells excitation. So far, for solid samples, the soft X-ray absorption spectroscopy has been utilized for the studies of developments for functional materials, the speciation of pollution compounds, the mechanistic analysis of catalytic reactions and vital functions [1]. However, for the soft X-ray absorption experiments for liquid samples, it has really been difficult to design the liquid cell system which is able to measure the absorption spectra under atmospheric pressure. In this paper, we report on a new liquid cell system for the soft X-ray absorption experiments developed at ALS, and show the X-ray absorption near-edge structure (XANES) spectra for aqueous Al salt solutions by the use of the cell system.

APPARATUS

The setup of the developed cell system is depicted in Figure 1. This cell system has been installed in BL6.3.1, and has the vacuum system with two shutters to keep the pressure in the path, ca. 10^{-7} Torr. The window attached the silicon nitride (Si_3N_4) membrane, which has 150 nm in thickness and 1 mm square, is fixed on the end of the pressure path. A liquid sample is trapped between two other Si_3N_4 membrane windows, on which the polystyrene microspheres (ca. 10 μm in diameter) are dropped in advance. The liquid sample trapped is fixed on the sample holder, which is made of stainless steel and designed as the beam is transmitted by the sample liquid and detected by the silicon photodiode under the optimal condition, and then it is put on the sample stage. The end of the pressure path, sample stage, and detector are covered with the acrylic case.

EXPERIMENTAL

Aluminum K-edge XANES spectra were collected by a transmission mode using the cell system for aqueous solution samples and by a total electron yield method for powder samples pressed onto the conductive carbon tape. The measured aluminum compounds were aluminum chloride (AlCl_3), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium aluminate, and aluminum ethylenediaminetetraacetate (Al-EDTA) complex. The aqueous solution of Al-EDTA was

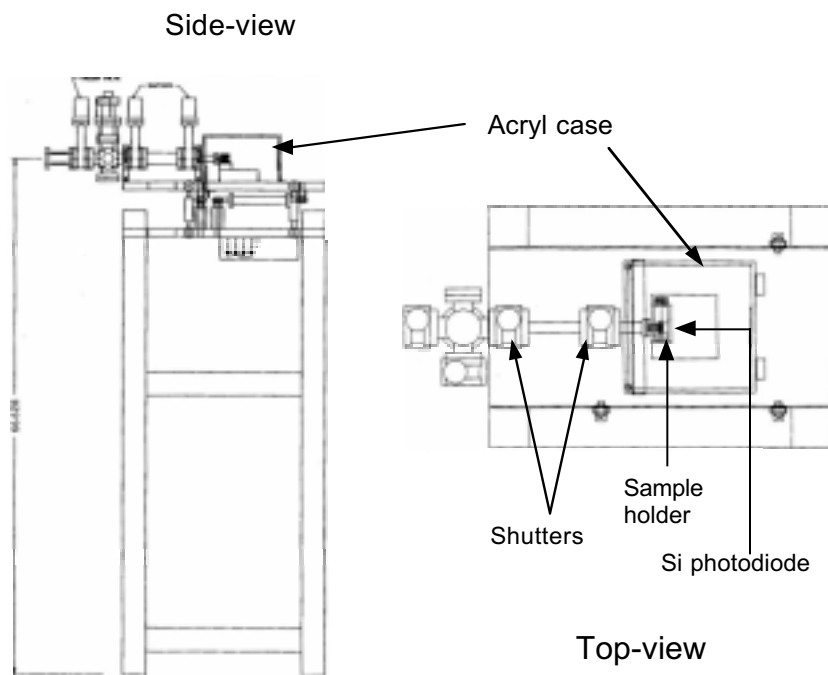


Figure 1. Setup of the XAFS cell system of soft X-ray absorption spectral measurements for solution samples.

prepared by adding 0.5 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ aqueous solution (25 ml) to 0.5 M EDTA tripotassium salt aqueous solution (25 ml) and finally adjusted to pH 4.5. The other solution samples were high-concentrated aqueous solutions. Al-EDTA sodium salt dihydrate was purchased from DOJINDO Laboratories. Data were collected from 1550 to 1620 eV at intervals of 0.2 eV with the speed of 0.5 s a point. In the measurements, Helium gas was made to flow and to fill in the acryl case, which was covered with a black cloth.

RESULTS

The Al K-edge XANES spectra for the aqueous solutions of AlCl_3 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, sodium aluminate, and Al-EDTA are shown in Figure 2 with those for their powder samples. In the powder samples, all the peak tops of the XANES spectra appear in almost similar energy position. In the aqueous solution samples, on the other hand, the peak tops of the XANES spectra of AlCl_3 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are similar in the position to those in their powder samples, while those of sodium aluminate and Al-EDTA are different from those in their powder samples, and shift to the low energy side. These results indicate that the coordination numbers for AlCl_3 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ little change between the powder and aqueous solution samples, and those for sodium aluminate and Al-EDTA show a change. In fact, by the NMR study the coordination number of Al-EDTA has

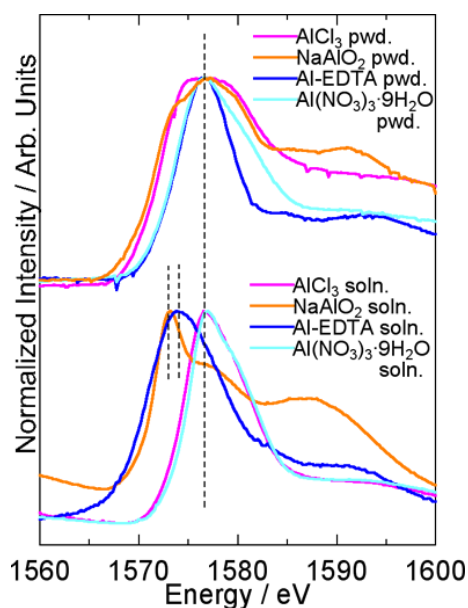


Figure 2. Al K-edge XANES spectra of powders and aqueous solution of various Al compounds.

been proposed to be six in powder and five in aqueous solution [2]. Accordingly, the peak position of the XANES spectra for Al-EDTA can be related with the coordination number. Furthermore, the relation between the peak position and coordination number would be also applied for all aluminum compounds.

CONCLUSION

The new liquid cell system for the soft X-ray absorption experiments developed at ALS enables us to record the spectra characteristic of chemical species in solution. For the XANES spectra of aqueous aluminum salt solutions obtained by the liquid cell system, the change of the peak position was related with the coordination structure, especially coordination number.

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Excitation-Energy Dependence of Cu $L_{2,3}$ X-Ray Emission Spectra of Cu, Cu₂O and CuO

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INTRODUCTION

Cu metal and its oxides have recently attracted considerable attention for the study of the electronic structure of copper oxides based on the superconducting matters. The Cu L X-ray emission spectra of Cu metal and its oxides have been measured by many laboratories for studying the electronic structure of the valence bands and the effect of chemical bonding on the satellites structure of the main peak of Cu $L\alpha_{1,2}$ X-ray emission using usual X-ray source [1,2] and synchrotron radiation [3-5]. The incident photon energy dependence was measured for Cu $L_{2,3}$ satellites using synchrotron radiation [3-5]. Changes in the Cu $L_{2,3}$ X-ray emission spectra with Cu metal and its oxides have been measured using electron excitation by Fischer [6]. He found that relative intensity $L\beta_1/L\alpha_{1,2}$ significantly depends on the incident electron energy and the target. The relative intensity $L\beta_1/L\alpha_{1,2}$ decreases with increase of excitation energy and it increases considerably for the oxides as compared to the metals.

In the present experiment, we have measured excitation-energy-dependence of Cu $L_{2,3}$ X-ray emission spectra of Cu, Cu₂O and CuO using synchrotron radiation in order to study the effect of chemical bonding in the excitation and deexcitation processes of inner-shell electrons of Cu metal and its oxides.

EXPERIMENT

The Cu (99.99 %) foil sample and sintered Cu₂O (99.9 %) and CuO (99.9 %) samples were commercially obtained. The spectral measurements in the Cu L region of these samples were performed at the beamline BL-8.0.1 for X-ray emission and fluorescence yield (FY) X-ray absorption measurements and at BL-6.3.1 for total-electron yield (TEY) X-ray absorption measurements.

In order to determine the excitation energies, XA spectra were measured by total electron-yields measurements. The incident photon current was continuously monitored using a gold mesh in

front on the sample to normalize the XE spectra.

RESULTS AND DISCUSSION

Cu $L_{2,3}$ X-ray emission (XE) spectra of Cu, Cu_2O and CuO spectra were measured at ten different excitation energies from 930~934 eV, at the L_3 threshold energy, up to energies as high as 990 eV, above the L_2 threshold energy. Figure 1 shows Cu $L_{2,3}$ XE spectra normalized to the integrated photon flux, excited at specific energies. The spectra were measured at 930~934 eV (L_3 threshold), at 950~952 eV (L_2 threshold), and at 990 eV (above the L_2 threshold). The relative intensity $L\beta_1/L\alpha_{1,2}$ significantly depends on the incident photon energy and the target. The intensity ratio for the Cu target is constant at any incident photon energy. On the other hand, those for the Cu_2O and CuO targets are the highest at the L_2 threshold energy, decrease abruptly just after the L_2 threshold energy, and then increase with the incident photon energy. This tendency is of interest from the view of the chemical effects on the excitation and deexcitation processes for inner-shell electrons.

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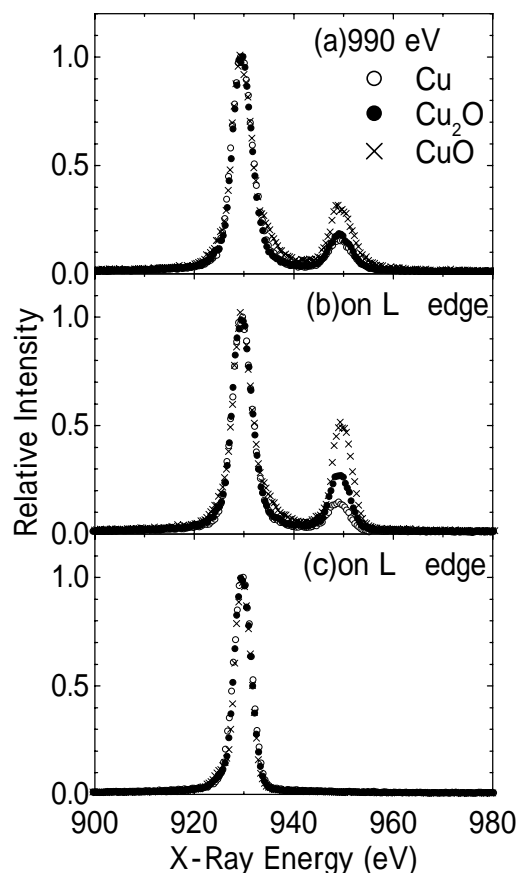


Figure 1. Comparison in the Cu L x-ray emission spectra of Cu, Cu_2O and CuO . Excitation energies are tuned at 990eV (a), L_2 (b) and L_3 (c) thresholds.

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